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TWO STEP MULTIVARIATE MODELING AND OPTIMIZATION OF SINTERING PROFILE OF ELECTRICAL CERAMIC FABRICATION PROCESS TO ENHANCE THE ELECTRICAL PROTECTION OF THE ELECTRONIC APPLIANCES

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Globally, billions of electronic devices are discarded due to their malfunction of low electrical protection from a non-linear property ceramic core varistor. The common varistor ceramic microstructure is made by the pressed powder of ZnO and small amount of additives such as Bi_2O_3, TiO_2, Co_3O_4, Mn_2O_3, Sb_2O_3 and Al_2O_3. The non-linearity is originated from the microstructure that is fabricated by a sintering profile. The profile is included sintering temperature, holding time, heating and cooling rate. In this work, the profile was modeled and optimized by multivariate method to enhance the non-linearity consequently improve the electrical protection. Therefore, two series of experiments were designed and were performed in laboratory to obtain the actual non-linear coefficient (α). The designs consisted of the sintering components and α as input variables and output response respectively. The actual results were used for two steps modeling of the ceramic fabrication's sintering profile. In the first step, the temperature and holding time of the sintering process were considered as input effective variables while heating and cooling rates were kept constant at 5 ˚C/min. However, the input of the process in the second step were heating and cooling rates at optimized temperature (1253^{o}C) and holding time (56 min). The outputs of the both steps were the calculated α that obtained from electrical characteristic of the fabricated ceramic. The results of performed design were used to model of the fabrication which was validated by analysis of variance. The validated model was used for determination of optimum value of the input variables that maximized α. Moreover, the model predicted a desirable condition of ceramic fabrication that was experimentally validated and used as final varistor ceramic. The ceramic was characterized by I-V characteristic to calculate α. The calculated α was 35.22 in first step while it was improved to 42.18 in the second step of modeling and optimization. In conclusion, the multivariate modeling and optimization which could be industrial scale up has been succeeded to promote the protection of electric and electronic devices.

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1. Introduction

Annually billions of electronic appliances are discarded around the world due to weak electrical protection from the overvoltage which are generated by electrostatic discharge and electrical overstress such as lightning strikes, power outages tripped circuits, power transitions, power malfunctions, electromagnetic pulses and inductive spikes in the associated circuit [1-2]. The electrical protection has been carried out by single and multi p-n junction back-to-back zener diodes and varistor devices respectively [3]. The diodes are able to control the lower unwanted voltage for several times while they unable to clamp the larger overvoltage due to their low capacity and single p-n junction [4]. On the other hand, the varistor tend to be more stable in AC and DC field over wide range of voltage, a few volts to tens kilovolts and current from micro-amperes to kilo-amperes.

The varistor is associated in parallel of the protected instrument and operates as an ohmic resistor in normal voltage while it presents non-linear behavior at the overvoltage [5]. The non-linearity is expressed by the terms of $I \propto V^{\alpha}$ where α is the non-linear coefficient [6-7]. To clamp the overvoltage, the high α is demanded. However, the α which is originated of used ceramic core in the varistor is very low that could be a big drawback for the electrical protection [8-9]. In the most common varistor, the ceramic core consists of highly conductive n-type zinc oxide (ZnO) grains that are surrounded by the narrow boundaries of the melted specific metal oxides as additives [10-11]. The normal additives are included Bi_2O_3, TiO_2, Co_3O_4, Mn_2O_3, Sb_2O_3 and Al_2O_3 which are used as formers and stabilizers in the mixed starting powder of the ceramic core microstructure [12-17]. In the microstructure, the mixed powder is pressed and then melted to occupy the ZnO grain boundaries by sintering process. The process affects the boundaries occupation as well as the composite of the melted additive that manage the quality of the protection through the certain volume of intrinsic oxygen vacancies transformation [3, 13, 18-25].

As reported, the α was decreased at low temperature, short holding time, fast heating and cooling rates as well as at higher temperature, longer holding time, slower heating and cooling rates [26-28]. The reduction at higher temperature, longer holding time, slower heating and cooling rate are due to additives evaporation while at lower temperature, shorter holding time, faster heating and cooling rate the melting of the additives may not be completed to occupy the grain boundaries. Therefore, the components of the sintering profile such as temperature, holding time, heating and cooling rates are the effective variables for the ceramic fabrication process. To enhance the α as output of the fabrication, it is crucial to optimize the effective variables. The optimization is usually carried out by the traditional techniques such as one variable at a time method. In the method, one of the inputs was varying while the other parameters are initially kept constant to measure the final response [29-30]. In this case, the variables are not completely independent during sintering process. Moreover, there are other complexities such as different reactions including formation and decomposition of many phases, kinetic of ZnO grain growth, densification of melted additives during the ceramic fabrication [28, 31]. Furthermore, the number of experiments is quite high due to the variety of the input additives which entail time consumption and possible misinterpretation of the related results. On the other hand, the multivariate methods such as response surface methodology (RSM) have been widely used for modeling and optimization of the productive process that is free of the mention complexity [32-35].

The modeling is taken place by using semi-empirical data including experimental results, and a group of mathematical and statistical techniques. In this work, the sintering process of ZnO based low voltage fabrication with four input effective variables and one response as final output was modeled by RSM. The obtained model was validated by statistical well-known techniques such as analysis of variance. The validated model was used to navigate the fabrication of the ceramic core varistor. In addition, the model predicted the desirable condition of sintering process with minimum standard error and the maximum α which was experimentally validated as final varistor ceramic. The microstructure of the final ceramic was characterized by X-ray Diffraction Analysis (XRD), Variable Pressure Scanning Electron Microscope (SEM).

2. Experiment

2.1 Materials and methods

The starting powder consisted of ZnO (99.99 %), Bi_2O_3 (99.975 %), TiO_2 (99.9 %), Co_3O_4 (99.7 %), Mn_2O_3 (98.0 %), Sb_2O_3 (99.6 %) and Al_2O_3 (99 %) which were provided from Alfa Aesar. The appropriate of the chemicals were mixed by ball milling in a plastic jar that contained zirconium balls, acetone and Na_2SiO_3 for 24 h. The obtained mixed powder was dried by oven for 8 h at 100 °C. Then 0.2g of the mixed powders was pressed at 200 MPa by unaxial processer machine. The pressed samples (pellets) were 11 mm in diameter and 0.7 mm of thickness. The pellets were sintered according to the experimental design (Tables 1 and 2) by a box furnace (CMTS model HTS 1400). The surfaces of the sintered samples were painted by silver electrodes to scan the DC current density-electric field (J-E). The scan was measured by Keithley 2400 source meter to calculate α for each sample. The scan range was determined from 0 to 100 volts in step size of 2.5 V. α of the samples was calculated at J_1= 0.1 and J_2 = 1 mA/cm^2 by equation 1[36],

$$Alpha = \frac{logJ_2 - logJ_1}{logE_2 - logE_1} \tag{1}$$

where E_1 and E_2 were measured at J_1 and J_2 respectively. The calculated α was used for fitting process. The J and E were obtained from the current I and voltage V divided by surface of the painted silver electrode (cm^2) and thickness of the ceramic core (mm) respectively. The final varistor ceramic was characterized by X-ray diffraction (XRD; PANanalytica, Philips-X'pert Pro PW3040/60) and field emission scanning electron microscopy (FESEM; JEOL JSM-7200) with energy dispersive X-ray analysis (EDX). The XRD was within the 2θ scan range of 20-80^o for the phase analysis.

Table 1. The sintering process experimental design for fabrication of the ceramic core in ZnO based low voltage varistor

Std	Temperature and holding time				Heating and cooling rates			
	Temp	Time	Alpha (actual)	Predicted	Heating rate	Cooling rate	Alpha (actual)	Predicted
1	1250	50	5.2	5.1	4	4	9	9.0
2	1270	50	8.1	7.9	7	4	7.72	7.8
3	1250	70	9.6	9.5	4	7	7.5	7.4
4	1270	70	5	4.9	7	7	9.5	9.5
5	1246	60	8.8	8.9	3	5.5	9	9.1
6	1274	60	7.4	7.6	8	5.5	9.7	9.7
7	1260	46	4.9	5.0	5.5	3	7.5	7.5
8	1260	74	5.9	6.0	5.5	8	7.5	7.6
9	1260	60	33.9	33.9	5.5	5.5	39.2	40.0
10	1260	60	34.2	33.9	5.5	5.5	40.1	40.0
11	1260	60	33.7	33.9	5.5	5.5	39.7	40.0
12	1260	60	33.5	33.9	5.5	5.5	40.3	40.0
13	1260	60	34.3	33.9	5.5	5.5	40.5	40.0

2.2 Experimental design and statistical analysis

Experiment of design (EOD) is carried out for semi-empirical modeling which uses actual responses and particular mathematic and statistical algorithms. As Table 1 shows, the design was carried out by central composite design (CCD) which embedded in the Design-Expert software version 8.0.7.1, Stat-Ease Inc., USA [37-38]. In the design, melting temperature, holding time, heating and cooling rate were considered as the input effective variables while α was only output response. Table 2 shows the variables in coded symbols as well as the actual values and ranges used in the design that identified. The central points are the replicated samples which were acquired to measure the experimental pure error. In the design, each raw shows the fabrication process of a varistor ceramic (Run) while the columns indicate the amount of the variables, the calculated and model predicted α of the each ceramic. The calculated α presented was used for the RSM fitting process to find the appropriate model which applied for optimization of the varistor ceramic[39-40].

Table 2. The effective variable in the sintering process and their used levels for experimental design

Effective variables		Level of the variables					
Coded	Actual	The lowest	Low	Center	High	The highest	Unit
x_1	Temperature	1246	1250	1260	1270	1274	^{o}C
x_2	Holding Time	46	50	60	70	74	Min
x_3	Heating rate	3	4	5	5.5	7	deg/min
x_4	Cooling rate	3	4	5	5.5	7	deg/min

2.3 The RSM fitting process

The fitting process uses the actual response (Table 1) to compare linear, two-factor interaction (2FI), quadratic and cubic models. In case of quadratic model, there is a second-degree polynomial such as E.q 2 that is popular for optimization process [41].

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \beta_{ij} x_i x_j + \varepsilon \tag{2}$$

where Y is the response value, β_0 is a constant coefficient, β_i is the linear coefficients, β_{ii} represents the coefficient of the quadratic terms, β_{ij} is the interaction coefficients while x_i is the coded value of the factors and 'ε' is a random experimental error [42]. In the fitting process, the coefficients of the all four models are estimated by by using sequential model sum of square (SMSS) [43]. The SMSS results the models are compared to suggest an appropriate mathematic equation as the provisional model of the process [44]. The suggestion is based on the comparison of statistical concepts such as adjusted R-squared (R_{Adj}), predicted R-squared (R_{pred}) and probability value (P-value) for SMSS and lack of fit. For SMSS, the small rate of p-value is considered when R_{Adj} and R_{pred} are at the maximum values while the concepts of 'Lack of fit' are vice versa [44-46]. The provisional model is deeply validated by analysis of variance (ANOVA) which determines the importance of terms of the model [47]. Then, the validated model is used to navigate the system that consists of the variables graphical optimization and importance of the effective variables as well as the model is able to predict the desirable condition that usually validates by further experiments.

3. Results and discussion

In this work the sintering process of the ceramic fabrication was modeled and optimized to improve α of final varistor ceramic as protector of electrical devices. The modeling process was carried out by semi-empirical method such as RSM. In the process the temperature, holding time, heating and cooling rate were the effective input variables while α of the final ceramics were the output. The obtained model was validated by statistical techniques then it used to navigate the fabrication which included optimization of the input variables to maximize the output as well as determined the importance of the input variables. Moreover, the models predicted the optimum condition of sintering process of the ceramic fabrication that was validated by further experiment. The electrical characteristics of the fabricated varistor ceramics were quit close to the prediction that confirmed the predictability of the model. The modeling was carried out in two steps and the optimum results of the first step were used for second step.

3.1 The modeling of sintering process

Table 3 shows the results of the sintering process modeling for 2FI, linear, quadratic, and cubic models which included to standard deviation (Std. Dev.), R-squared (R^2), R_{Adj}, R_{Pred}, SMSS and lack of fit. As shown, the quadratic model has presented the highest R^2, R_{Adj} and R_{Pred} in the both steps. Moreover, the model showed significant SMSS with the highest F-value and the lowest p-value while the values of these parameters were vice versa for lack of fit. When the lack of fit is not fit, it means the model is well fit. For that reasons, the quadratic model was provisionally suggested for more investigation which carried out by ANOVA.

Table 3. The model summary statistics results of the 2FI, linear, quadratic and cubic models, Std.Dev. is standard deviation and SMSS is sequential model sum of square

Source	Model	Std.Dev.	R^2	R_{adj}	R_{pred}	SMSS		Lack of Fit		Remark
						F-value	p-value	p-value	F-value	
First step	Linear	15.1	0.001	-0.1986	-0.575	0.01	0.9943	< 0.0001	3384	
	2FI	15.8	0.007	-0.3236	-1.191	0.06	0.8182	< 0.0001	4036	
	Quadratic	0.3	1.000	0.9996	0.999	14108	< 0.0001	0.8019	0.34	Suggested
	Cubic	0.3	1.000	0.9994	0.997	0.05	0.9498	0.3955	0.90	Aliased
Second step	Linear	17.512	0.000	-0.200	-0.572	0.001	0.9994	1906	< 0.0001	
	2FI	18.451	0.001	-0.332	-1.218	0.008	0.9311	2286	< 0.0001	
	Quadratic	0.395	1.000	0.999	0.999	9826	< 0.0001	0.024	0.9943	Suggested
	Cubic	0.463	1.000	0.999	0.999	0.044	0.9572	0.000	0.9898	Aliased

3.2 Model validation

Table 4 depicted the ANOVA information of the terms in suggested quadratic models including Eq's 3 and 4 for sintering process. As the detail of validation, the term's partial sum of squares has confirmed the significance of x_1, x_2, x_1x_2, x_1^2 and x_2^2 in the first step model while the parameters of second step model including x_3 and x_4 were not significant. It means x_3 and x_4 were unimportant in the second step model.

$$Y = -205905 + 325.00x_1 + 40.70x_2 - 0.02x_1x_2 - 0.13x_1^2 - 0.14x_2^2 \quad (3)$$

$$Y = -374 + 72.96x_3 + 77.36x_4 + 0.36x_3x_4 - 6.81x_3^2 - 7.21x_4^2 \quad (4)$$

where x_1, x_2, x_3 and x_4 are codes of the input variables of sintering process which were identified by Table 2. In the models, the linear term and interaction terms were x_1, x_2, x_3, x_4 and x_1x_2, x_3x_4 respectively which have synergic effect on the alpha. However, the quadratic terms such as x_1^2, x_2^2, x_3^2 and x_4^2 have an antagonistic effect on the alpha. The importance of the models' terms is determined by the coefficients of them in the models. The importance priority of the terms in first step were $x_1 > x_2 > x_2^2 > x_1^2 > x_1x_2$ while the priority in second steps was $x_4 > x_3 > x_4^2 > x_3^2 > x_3x_4$. As the result of the validation shown, the quadratic model has been recognized as outstanding final model which used to navigate the sintering process of ceramic fabrication.

Table 4. The ANOVA importance of the model's terms in first and second stem of quadratic model for the sintering process

First step				Second step			
Source	F-Value	p-value	Remark	Source	F-Value	p-value	Remark
x_1	21.1	0.0025	Significant	x_3	2.345126	0.1695	not-Significant
x_2	11.5	0.0116	Significant	x_4	0.06288	0.8092	not-Significant
x_1x_2	175.6	< 0.0001	Significant	x_3x_4	17.25748	0.0043	Significant
x_1^2	14349.6	< 0.0001	Significant	x_3^2	10453.88	< 0.0001	Significant
x_2^2	17522.1	< 0.0001	Significant	x_4^2	11755.79	< 0.0001	Significant

3.3 The model application

3.3.1 Optimization

The models are able to optimize the sintering process by using local optimum and graphical three dimensional plots (3D plot). The local optimum was obtained by differentiating of the both models (Eq. 3 and 4) that were presented by Eq. 5 to Eq. 8.

$$\left(\frac{\partial Y}{\partial x_1}\right)_{X_2} = 0 \tag{5}$$

$$\left(\frac{\partial Y}{\partial x_2}\right)_{X_1} = 0 \tag{6}$$

$$\left(\frac{\partial Y}{\partial x_3}\right)_{X_4} = 0 \tag{7}$$

$$\left(\frac{\partial Y}{\partial x_4}\right)_{X_3} = 0 \tag{8}$$

where the terms were identified by Table 2. In fact, this optimization which determines the optimum point values is one-variable-at-a-time method that varies one of the factors while others keep constant. However, in graphical optimization, the effect of two variables on the alpha was considered simultaneously. Fig. 1 shows the 3D and counter plot of sintering temperature (1250-1270 °C) and holding time (50-70 min) which simultaneously affect the alpha. As observed, the alpha increased slightly within 1250 to 1260°C for sintering temperature as well as 50 to 60 min for holding time. However, with increasing the amount of sintering profile excess of the optimum, the α value dramatically decreased. It attributed to additives vaporization at higher sintering temperature [38, 48-50]. The maximum α was 33.92 at center of 1260°C and 60 min which indicated by the flag on the 3D plots (Fig. 1). In first step, the model (Eq. 3) was used to predict the desirable condition which included the minimum value of sintering temperature, holding time and standard error while α was maximum value. As a result, the predicted condition was sintering temperature (1253°C), holding time (56 min), standard error (0.096), and α 35.22 that it was validated by further experience. The predicted condition was performed to fabricate a sample as final ceramic and then it was evaluated J-E characterization. The obtained value of J-E characteristic showed α 35.01 that it is very close to the model predicted value. The condition was based for second step modelling and optimization.

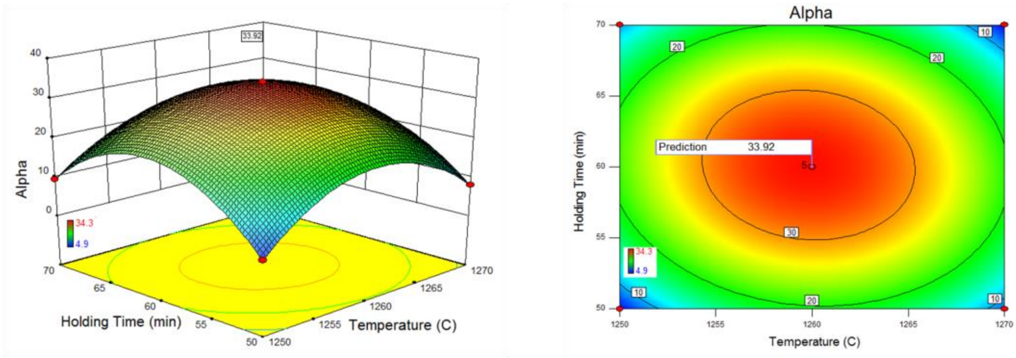

Fig. 1. The 3D and counter plot of sintering temperature and holding time against to the alpha of the low voltage varistor ceramic

Fig. 2 shows the 3D and counter plot of sintering heating and cooling rates of the sintering process (4-7 ˚C/min) that simultaneously affect the α. As showed, α was increased slightly with increasing the rates up to 5.5 ˚C/min then it dramatically was decreased. As indicated, α 39.96 that it was enhanced in comparison with first step of optimization. As conclusion, the optimum points of the input variables were around sintering- temperature (1260°C), holding time (60 min), heating and cooling rate (5.5 ˚C/min) which confirmed that the initial selected levels of input variables were quit wide. Therefore, the second step model was used to predict the final desirable condition instead of re-design the project.

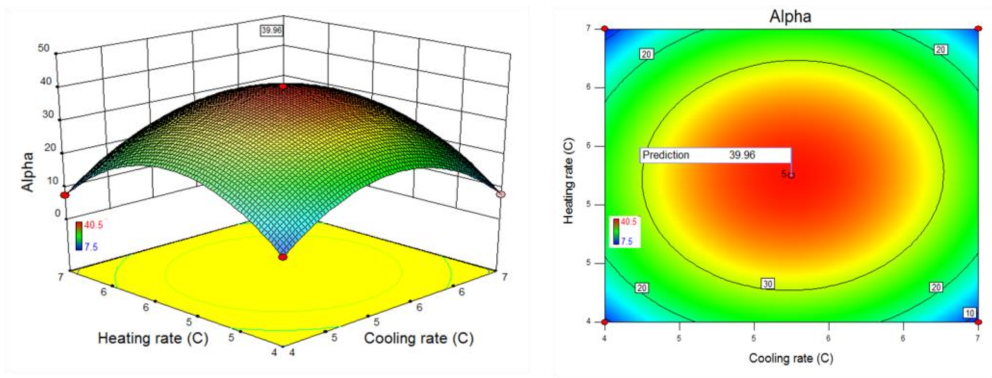

Fig. 2. The 3D and counter plot of the sintering process heating and cooling rate against to the alpha of the low voltage varistor

3.3.2 Model prediction as final varistor ceramic

The second step model predicted a varistor ceramic with maximum α at high desirability value by using numerical option. The desirability is an objective function that uses mathematical methods, where the range of the desirability starts from zero for out of the limited area and goes to one at the goal methods [51]. The desirability of this prediction was 0.89 that was very close to the goal. The options were facilitated by the software which allows experiment to select a particular condition. In this case, the amount of the heating rate and cooling rate were selected 'in range' for minimum 'standard error' and maximum α. Then, model predicted a condition with 5.5 ˚C/min for both heating and cooling and standard error was 0.021 while the proposed α was 41.82. The predicted condition was experimentally fabricated and then electrically characterized as final ceramic. The result of the electrical characterization obtained high value (42.18) which is very close to the model prediction. For more information, the element analysis and morphology of the ceramic core microstructure in the varistor ceramic was investigated by XRD and SEM respectively. Fig. 3 shows the XRD element analysis of the ceramic core microstructure in the final ceramic. As shown, the pattern has confirmed presence of all elements that used in the initial additives as starting powder in different form of material such as spinel structure. The presentation proved that the additive did not completely evaporate during sintering process that means the optimized condition might be suitable for the varistor ceramic fabrication.

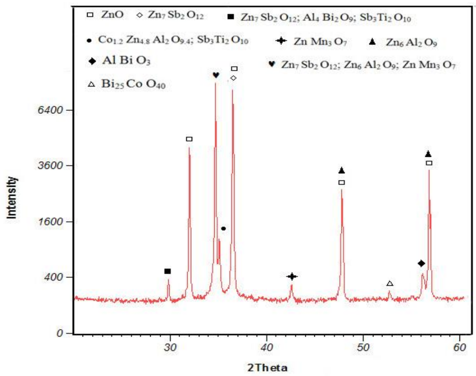

Fig. 3. The XRD pattern of the final varistor ceramic that fabricated at optimized condition of sintering profile such as temperature, 1253, holding time, 56 min, heating and cooling rates 6 ^{o}C/min with α, 42.18

Fig. 4 illustrates the SEM morphology of the ceramic core microstructure that used in the final optimized ceramic. As indicated, the grains of ZnO in the microstructure were homogeneous size distribution which confirmed the optimized holding time in the sintering process. Moreover, the grains boundaries were filled up of the melted additives that are shown effectiveness of the sintering process.

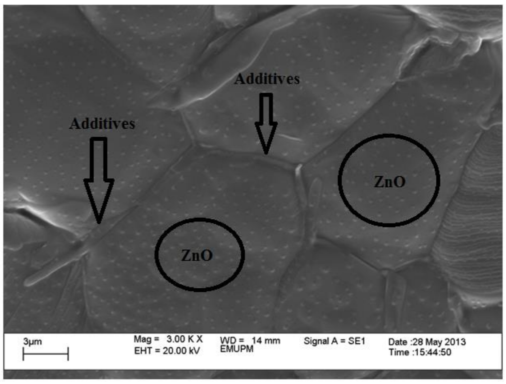

Fig. 5. The SEM morphology of the ceramic core microstructure used in final optimized varistor ceramic with α, 42.18, at sintering profile such as temperature, 1253 ^{o}C, holding time, 56 min, heating and cooling rates 6 ^{o}C/min

4. Conclusions

In this work, two steps modeling and optimization of the varistor ceramic core fabrication sintering process was carried out to improve the protectiveness of electrical devices by RSM as semi-empirical and multivariate method. In the first step, the temperature and holding time of the sintering process were considered as input effective variables while heating and cooling rates were kept constant at 5˚C/min. However, the input of the process in the second step were heating and cooling rates at optimized temperature (1253^{o}C) and holding time (56 min). The output of both steps was the calculated α which obtained from electrical characteristic of the fabricated ceramic. The model was obtained by fitting process of performed design which was validated by ANOVA.

The validated model was used for determination of optimum value of the input variables that maximized α. Moreover, the model predicted a desirable condition of ceramic fabrication that was experimentally validated and used as final ceramic. It was characterized by J-E characteristic to calculate α. The calculated α was 35.22 in first step while it was improved to 42.18 in the second step of modeling and optimization. In conclusion, the multivariate modeling and optimization which could be industrial scale up has been succeeded to promote the protection of electric and

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